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Modification of High Potential, High Capacity $Li_2FeP_2O_7$ Cathode Material for Lithium Ion Batteries

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ABSTRACT

$Li_2FeP_2O_7$ is a newly developed polyanionic cathode material for high performance lithium ion batteries. It is considered very attractive due to its large specific capacity, good thermal and chemical stability, and environmental benignity. However, the application of $Li_2FeP_2O_7$ is limited by its low ionic and electronic conductivities. To overcome the above problem, a solution-based technique was successfully developed to synthesize $Li_2FeP_2O_7$ powders with very fine and uniform particle size (< 1 μm), achieving much faster kinetics. The obtained $Li_2FeP_2O_7$ powders were tested in lithium ion batteries by measurements of cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge cycling. We found that the modified $Li_2FeP_2O_7$ cathode could maintain a relatively high capacity even at fast discharge rates.

INTRODUCTION

Lithium ion batteries (LIBs) are widely used as power sources in portable computers, entertainment devices, telecommunications, and recently electrical automobiles. As required by EV (electrical vehicles) and HEV (hybrid electrical vehicles), LIBs should be able to store and release large amount of energy in a short time length, while of light-weight. Therefore, large-scale production of novel cathode materials, with high voltage and large specific capacity, were urgently demanded. Currently available cathode materials such as $LiCoO_2$ [1] and $LiFePO_4$ [2] couldn't fulfill these requirements very well, mostly limited by high price and relatively low specific capacity.

A lot of research has been conducted on polyanionic cathode materials. One way of increasing specific capacity is to increase the redox potential of the polyanionic $LiMXO_4$ (M: transition metal; X = P, As, Si, Ge) [3-6]. Though there has been a large amount of work done on this topic, the overall performance of these materials is not significantly greater than that of more traditional cathode materials. Another way of achieving high specific capacity is to increase the number of removable lithium atoms in one formula. For this purpose, extensive studies have been focused on $Li_xM'_2(YO_4)_3$ (x > 1, M': transition metal; Y: S, P, Mo), leading to the development of $Li_2FeP_2O_7$ [7]. Although $Li_2FeP_2O_7$ (LFPO) has low electronic and ionic conductivity, it has a theoretical capacity of 220 mAh/g with both lithium atoms extracted, even higher than that of $Li_3V_2(PO_4)_3$ which can remove three lithium atoms. [8-10] Therefore, it is desirable to synthesize LFPO with improved kinetic properties.

In this paper, we are reporting the modification of LFPO synthesized through a solution-based technique. The effect of synthesis parameters on the crystal structure, morphology and electrochemical performance of the LFPO powders was thoroughly studied.

EXPERIMENTAL DETAILS

Stoichiometric amount of precursor materials were first dissolved in de-ionized water and mixed together; then ammonium hydroxide was added in, and a transparent solution was achieved at the PH value of 4. The solution was then transferred into a flask and refluxed overnight. After that, the solution was evaporated on a hot-plate and concentrated to a gel, which was then dried at 90 °C in a vacuum. Following that, the sample was placed in a tube furnace and heated at 350 °C for 5 hours under a nitrogen atmosphere, resulting in powders that were then ground and pressed into pellets. At last, the pellets were annealed at different temperatures (500, 550 and 600 °C) for 24 hours in nitrogen. The precursor materials used in the experiment were $LiOH{\cdot}H_2O$, P_2O_5, $Fe(NO_3)_3{\cdot}9H_2O$ and $C_6H_8O_7$ (citric acid). The $LiOH{\cdot}H_2O$ to $C_6H_8O_7$ molar ratio was initially set to be 1: 1.

The obtained samples were characterized on a Philips PW 3040 X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å) at the 2θ range of 10° - 90° with a step size of 0.015° and a step time of 0.6 seconds. The scanning electron microscopy (SEM) images were taken at an operating voltage of 20 kV and a working distance of ~15 mm.

The LFPO samples were made into a cathode and tested in lithium ion batteries. The cathode was fabricated firstly by forming a slurry, which was a mixture of LFPO with PVDF binder (polyvinylidiene fluoride) and carbon black at a weight ratio of 85: 5: 10 in an NMP solvent (N-methyl-2-pyrrolidone). The slurry was then tape-casted on an aluminum foil and baked overnight in a vacuum, with a mass loading of around 10 mg/cm^2. The batteries were assembled in an argon filled glove box, using lithium metal as the anode, Celgard 2400 as the separator, and 1 M $LiPF_6$/EC-DEC (1:1 vol %) as the electrolyte. The charge/discharge cycling of the cells was tested between 2 V and 4.5 V at different rates from C/20 to 5C. The electrochemical impedance spectroscopy (EIS) was measured in a frequency range of 1 MHz to 0.4 Hz. The cyclic voltamegram (CV) of the cells was scanned from 2 V to 5 V at a rate of 0.05 mV/s.

DISCUSSION

X-ray diffraction

Figure 1 shows the XRD patterns of the samples annealed at different temperatures (500 °C, 550 °C and 600 °C). At 500 °C, the sample is likely monoclinic with very broad peaks. When heated at 550 ^oC, the powders show a typical XRD pattern for monoclinic LFPO crystals, which belong to the $P2_1/C$ space group. Plus, the peaks are sharp, indicating good crystallinity. When annealed at 600 °C, several extra peaks were observed for impure phases which might be $LiFeP_2O_7$, etc. Based on these results, we can tell that the annealing temperature has a great effect on the crystalline structures of the samples, and the best value found in our experiment is 550 ^oC. The lattice constants of the monoclinic LFPO crystals were calculated to be a = 11.0196 Å, b = 9.7497Å, and c = 9.8058 Å, β = 101.5011 °, which were consistent with the literature. [7]

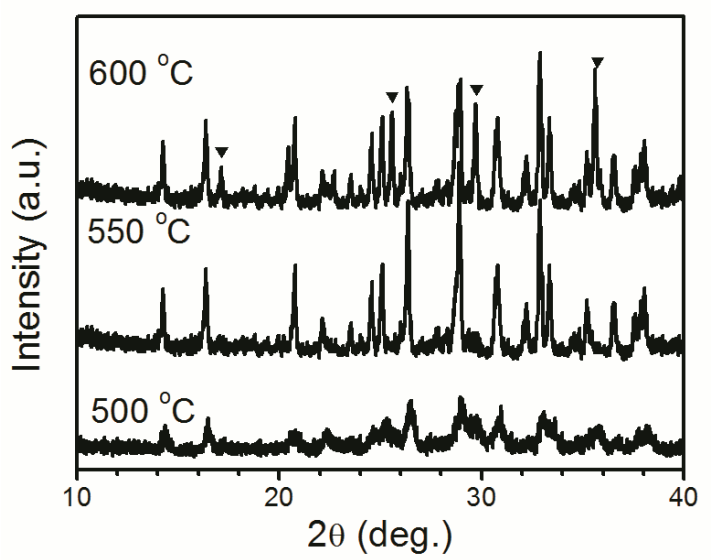

Figure 1. XRD patterns of LFPO powders annealed at 500 °C, 550 °C, and 600 °C

Scanning electron microscopy

The LFPO powders annealed at 550 °C had a large particle size of ~2 μm (sample 1), as shown in Figure 2a. Further reduction of the particle size is needed in order to enhance the kinetic properties of the LFPO powders. As we know, citric acid acts as the chelating agent in the sol-gel process and produces reductive atmosphere during gel-to-powder transformation. Moreover, the residual carbon can restrain grain growth and particle agglomeration during sintering by distributing uniformly between grains [11]. For this, proper amount of citric acid was added to the starting solution, obtaining a $LiOH{\cdot}H_2O$ to $C_6H_8O_7$ Molar ratio of 1: 1.5 (M_{Li}: M_{C6} = 1: 1.5). The SEM image of the newly obtained LFPO powders (sample 2) is shown in Figure 2b, where we can see the particle sizes become very uniform and most of them are smaller than 1 μm.

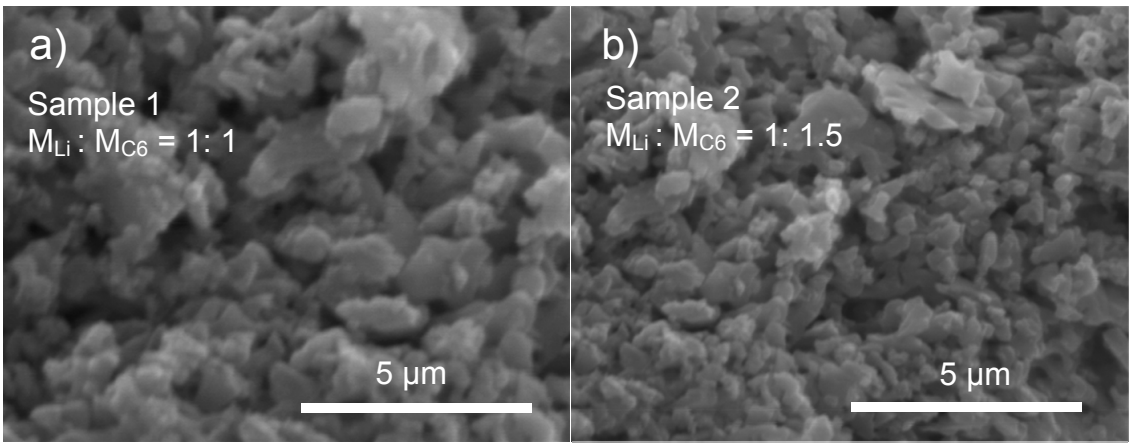

Figure 2. SEM images of the **(a)** pre-modified and **(b)** modified LFPO powders

Electrochemical impedance spectroscopy

Figure 3a shows the electrochemical impedance spectroscopy (EIS) of the lithium ion batteries as-assembled using sample 1 and sample 2 as the cathode, respectively. The curves can be fitted into the equivalent circuit drawn in the figure: R_e (C_{dL} // ($R_{ct}Z_w$)) C_L (e: electrolyte; ct: charge transfer; w: Warburg diffusion; dL: double layer; L: intercalation capacity). [12] The charge transfer resistance was largely reduced for the smaller size LFPO particles, due to larger surface areas. Figure 3b shows the EIS results of the cells after the first charge process. The curves can be fitted by an equivalent circuit model (inserted diagram): Re (C_{sf}//R_{sf})(C_{dl}//R_{ct})Z_w (sf: surface layer). Still, the finer size LFPO cathode displayed smaller inner resistances in the charged cells. Batteries of small inner resistances are expected to exhibit higher capacity, faster charge/discharge rates, and smaller potential polarization.

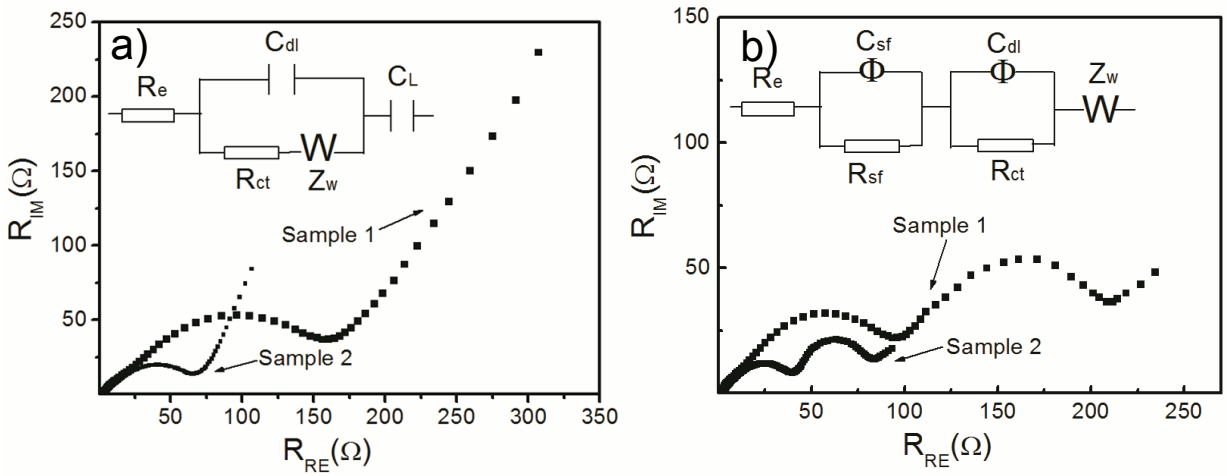

Figure 3. (**a**) EIS and equivalent circuit of the as-assembled lithium ion cells; (**b**) EIS and equivalent circuit of the cells charged after the first time

Cyclic voltammetry

The cyclic voltammetry of the cells were measured, and the results are shown in Figure 4. The cells exhibit a strong anodic peak around 3.5 V and a consequent cathodic peak at 3.2 V. The rising part around 5 V was assigned to the Fe^{3+}/Fe^{4+} oxidation at 5.2 V, as predicted by Whittingham's group. [13] A small anodic peak at 4.5 V was observed, which may be caused by the removal of lithium atoms from a type of location that requires more energy (higher voltage) for the ionization of one lithium atom. Further research on the structure of LFPO is needed to answer this question. Comparing the peak height of the two kinds of cells, the one with sample 2 as the cathode would display deeper reaction and higher capacity during charge/discharge process.

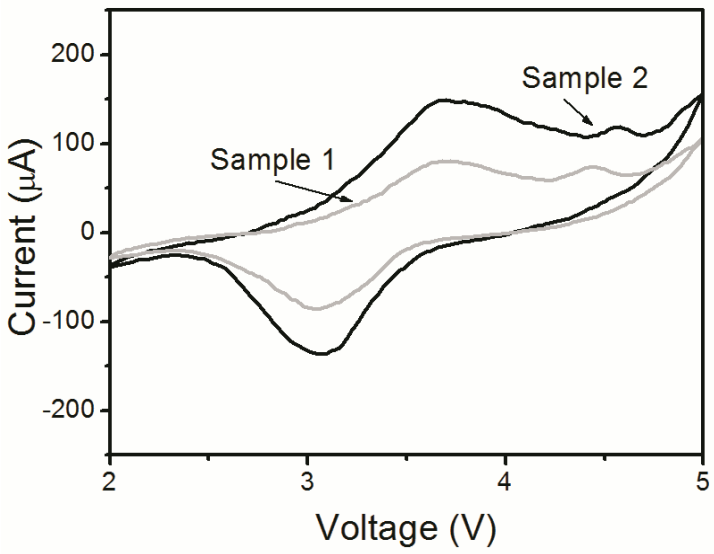

Figure 4. Cyclic voltammegrams of the cells scanned at a rate of 0.05 mV/S

Charge/discharge cycling

The charge/discharge behavior of these two kinds of cells is presented in Figure 5a and 5b, respectively. As expected, the cell with the modified cathode has a larger specific capacity of 106 mAh/g at the rate of 0.05 C, much higher than 82 mAh/g of the other cell. Moreover, the specific capacity of the modified LFPO cathode was larger for all rates in the range from 0.05 C up to 5 C, due to faster transport kinetics through the submicron LFPO powders.

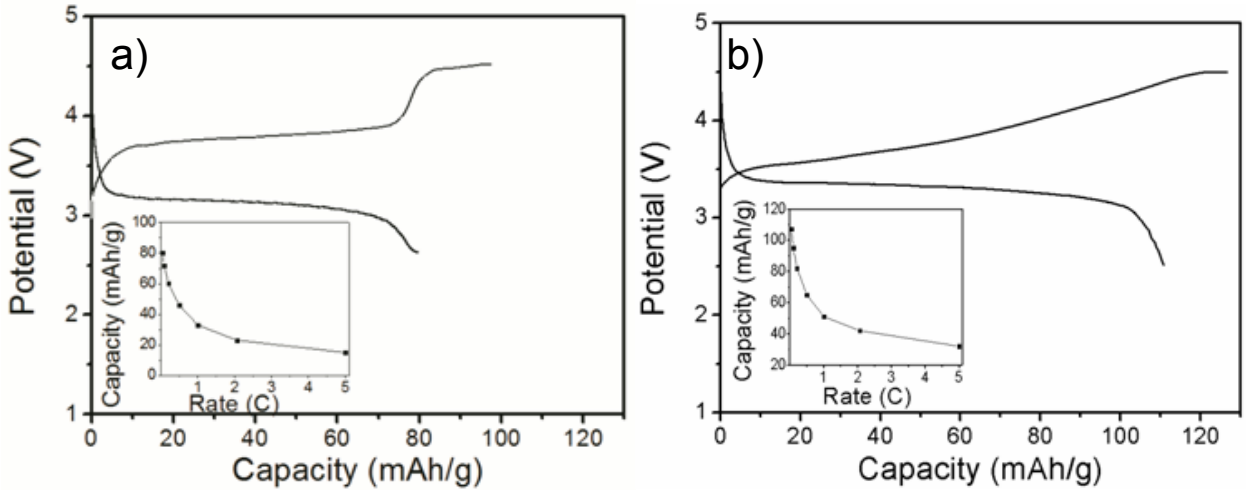

Figure 5. Cycling performances of the cells made with **(a)** sample 1 and **(b)** sample 2 as the cathodes

CONCLUSIONS

We have successfully synthesized and modified the novel LFPO cathode material using a solution-based technique. LFPO powders annealed at 550 °C possessed a pure monoclinic phase.

Two kinds of LFPO powders were synthesized with different particle sizes. The smaller particles resulted in reduced inner resistance and enhanced specific capacity of 106 mAh/g tested from lithium ion cells. Moreover, the cyclic voltammetry test proved that the second lithium of LFPO was active and removable; therefore, higher capacity is attainable for LFPO when coupled with an electrolyte of proper voltage window.

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